A process for the production of polychloroprene mixtures of sol and gel polymers in a ratio, by weight, of 1:4 to 9:1, the gel polymer being produced by radical emulsion polymerization from chloroprene in the presence of 4 to 10% by weight of water soluble disproportionated abietic acid, and the sol polymer being produced by radical emulsion polymerization of chloroprene in the presence of not more than 3.5% by weight of a water soluble disproportionated abietic acid with the polychloroprene mixture containing at most 3.8% of said acid.
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PROCESS FOR THE PRODUCTION OF
CHLOROPRENE POLYMER MIXTURES

This invention relates to a process for the precipitation-
free polymerisation of chloroprene in aqueous
emulsion in the presence of defined quantities of emulsi-
ifier to form stable, storable latices and solid rubbers of
which the raw material and vulcanisate properties are
largely unaffected by the age of the latex.

In order to broaden the scope of application of polychloroprene rubbers, it is necessary to improve the
processibility thereof. Processibility is to be understood
to include, for example, a high injection capacity on
extrusion, minimal swelling on extrusion and high di-

mensional stability of the extrudates.

Polychloroprene rubbers having these properties may be produced by mixing benzene-soluble polychloroprene latex (sol polymer) and gel-containing pol-
chloroprene latex (gel polymer) and working-up the
resulting mixture, for example by low temperature co-
agulation, to form the solid rubber.

Such production processes are described in DE-AS
No 1,720,107 and in GB-PS No. 1,158,970. However, the improvement in processibility is achieved at the
expense of numerous disadvantages, for example poor
stability of the gel-containing latex in storage, poor
viscosity stability of the crude rubber and tensile
strengths of the vulcanisates which are considerably
poorer than those of the sol polymers.

German Auslegeschrift Nos. 2,008,673 and 2,241,394
propose various measures for avoiding this undesirable
deterioration in properties. These measures have only
been partially successful. In particular, it has not been
possible to overcome the marked dependence of the
viscosity stability of the crude rubber and the tensile
strength of the vulcanisates upon the age of the latex, particularly its gel component.

It has now been found that it is possible to produce
storabe, cross-linked polychloroprene latices which,
after mixing with sol polymers and working-up, give solid rubbers of which the raw material and vulcanisate
properties are largely unaffected by the age of the pol-

cloroprene latex.

Accordingly, the present invention relates to a pro-
cess for the production of polychloroprene mixtures of
sol and gel polymer in a ratio, by weight, of from 1:4 to
9:1, the gel polymer being produced by radical emulsion
polymerisation from chloroprene and from 1 to 4 mole
percent, based on the molar quantity of chloroprene,
of a diester of a dihydric alcohol and an acrylic acid in the
presence of a water-soluble saturated or unsaturated
monocarboxylic acid, in the presence of a condensation
product of naphthalene sulfonic acid and formalde-
hyde and in the presence of potassium hydroxide and the
sol polymer being produced by radical emulsion
polymerisation from chloroprene in the presence of a
water-soluble, saturated or unsaturated monocarboxylic
acid, in the presence of a condensation product of naph-
thalene sulfonic acid and formaldehyde and in the
presence of potassium hydroxide, characterised in that
the quantity of water-soluble, saturated or unsaturated
monocarboxylic acid used in the production of the gel
polymer amounts to from 4 to 10%, by weight, based on
the monomer total, in that the quantity of water-soluble
saturated or unsaturated monocarboxylic acid used in
the production of the sol polymer does not exceed
3.5%, by weight, based on the monomer total, and in

that the polychloroprene mixture contains at most
3.8%, by weight, based on the monomer total, of water-
soluble saturated or unsaturated monocarboxylic acid.

The diester preferably corresponds to the following
general formula:

\[
H_2C\overset{\text{O}}{\text{C}}\overset{\text{C}}{\text{C}}\overset{\text{O}}{\text{X}}\overset{\text{C}}{\text{C}}\overset{\text{O}}{\text{C}}\overset{\text{CH}_2}{\text{R}}_1 \\
\]

wherein

- R1 and R2 independently represent hydrogen or C1-C4
  alkyl;
- X represents C2-C10 alkylene.

The water-soluble saturated or unsaturated monocar-
boxylic acid used is, in particular, disproportionated
abietic acid, optionally in admixture with a fatty acid
such as oleic acid.

The water-soluble saturated or unsaturated monocar-
boxylic acid serves as emulsifier. The limitation to
3.8%, by weight, in the polychloroprene mixture is
necessary to avoid undesirably high tackiness on the
mixing rolls. This advantage becomes particularly clear
if the emulsifier content is particularly high during pro-
duction of the gel polymer and correspondingly low
during production of the sol polymer. The emulsifier is
preferably used in a quantity of from 4.6 to 6.0%, by
weight, in the production of the gel polymer and in a
quantity of from 1.2 to 3.4%, by weight, in the produc-
tion of the sol polymer.

Polymerisation of the two components may be car-
ried out continuously or in batches, continuous
polymerisation being preferred. Polymerisation is car-
ried out by the conventional methods of the type de-
scribed, for example, in German Auslegeschrift Nos.
1,720,107; 2,008,673 and 2,650,714. Working-up by
low-temperature coagulation may be carried out, for ex-
ample, by the method described in German Auslegeschrift
No. 1,051,606.

The quantity of condensation product of naphthalene
sulfonic acid and formaldehyde preferably amounts to
from 0.3 to 1.0%, by weight, while the quantity of po-
tassium hydroxide preferably amounts to from 0.4 to
1.0%, by weight, based in each case on the monomer
total.

50% of the potassium ions may be replaced by other
alkali metal ions.

COMPARISON EXAMPLE 1 (Sol polymer)

The aqueous phase W and the monomer phase M
were initially introduced into a coolable reaction vessel
and the activator phase A continuously introduced
thereafter:

<table>
<thead>
<tr>
<th>Monomer phase M</th>
<th>Chloroprene</th>
<th>n-dodecyl mercaptan</th>
<th>Deionised water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100.0 g</td>
<td>0.22 g</td>
<td>130.0 g</td>
</tr>
<tr>
<td>Potassium salt of disproportionated abietic acid</td>
<td>3.5 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium salt of the condensation product of naphthalene sulfonic acid and formaldehyde</td>
<td>0.7 g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The reaction begins readily at an internal temperature of 40°C. The heat of polymerisation given off is dissipated by external cooling and the polymerisation temperature maintained at +45°C. The reaction is terminated at a monomer conversion of 66% by the addition of phenothiazine. The residual monomer is removed from the polymer by steam distillation and the polymer latex stored at 10°C.

**COMPARISON EXAMPLE 2 (Gel polymer)**

The procedure is as in Example 1 using the following quantities:

<table>
<thead>
<tr>
<th>Monomer phase M₁</th>
<th>Chloroprene</th>
<th>Ethylene glycol dimethacrylate</th>
<th>n-dodecyl mercaptan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96.0 g</td>
<td>4.0 g</td>
<td>0.3 g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aqueous phase W₁</th>
<th>Deionised water</th>
<th>Potassium salt of disproportionated abietic acid</th>
<th>Potassium salt of the condensation product of naphthalene sulphonic acid and formaldehyde</th>
<th>Potassium hydroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>130.0 g</td>
<td>2.2 g</td>
<td>0.7 g</td>
<td>0.4 g</td>
</tr>
</tbody>
</table>

The reaction is terminated at a monomer conversion of 80% by the addition of phenothiazine. The residual monomer is removed from the polymer by steam distillation. The polymer latex is stored at +10°C.

**COMPARISON EXAMPLES 3–7 (Different quantities of emulsifier)**

The gel and sol polymer latices are prepared in the same way as in Examples 1 and 2 in the presence of different quantities of emulsifier, stored for 10 days, the gel polymer latex mixed with the sol polymer latex in a weight ratio of 40:60 and the rubber isolated.

**EXAMPLES 8 and 9**

The gel polymer latex and sol polymer latex are prepared in the same way as in Examples 1 and 2 in the presence of different quantities of emulsifier, stored for 10 days, the gel polymer latex mixed with the sol polymer latex in a ratio of 40:60 and the rubber isolated.

**Determination of viscosity stability**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>M.L-4 (3 days/70°C)</th>
<th>Δ M.L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>53</td>
<td>+26</td>
</tr>
<tr>
<td>4</td>
<td>51</td>
<td>+22</td>
</tr>
<tr>
<td>5</td>
<td>54</td>
<td>+4</td>
</tr>
<tr>
<td>6</td>
<td>51</td>
<td>+5</td>
</tr>
<tr>
<td>7</td>
<td>53</td>
<td>+4</td>
</tr>
<tr>
<td>8</td>
<td>53</td>
<td>+4</td>
</tr>
<tr>
<td>9</td>
<td>53</td>
<td>+5</td>
</tr>
<tr>
<td>10</td>
<td>53</td>
<td>+4</td>
</tr>
</tbody>
</table>

After working-up to form the rubber, the Mooney viscosity of the test specimens is determined (DIN 53523).

To determine viscosity stability, the test specimens are stored for 3 days at 70°C and the viscosity thereof measured again. The more stable the products, the smaller the difference in viscosity (Δ M.L) between the two measurements.

**Determination of tackiness on mixing rolls/calender test**

The reduced tackiness on mixing rolls of the polymers according to the present invention is demonstrated by a semi-practical test. The following substances are initially mixed over a period of 4 minutes in a laboratory kneader:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>100 g</td>
</tr>
<tr>
<td>Carbon black N-472</td>
<td>30 g</td>
</tr>
<tr>
<td>Aromatic mineral oil</td>
<td>15 g</td>
</tr>
<tr>
<td>Phenyl-c-naphthylamine</td>
<td>1 g</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5 g</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>4 g</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5 g</td>
</tr>
</tbody>
</table>

After storage for about 24 hours at room temperature the mixture is preheated to from 50°C to 55°C on mixing rolls and then drawn out to form a 0.3 mm thick band on a three-roller laboratory calender (roller length 400 mm; roller diameter 200 mm) with friction ratios of 1:1.31 between the 1st and 2nd rollers and 1:1 between the 2nd and 3rd rollers. Assessment of tackiness:

1 = sheet does not stick (is not entrained by the faster roller)
2 = sheet sticks slightly (is entrained to a certain extent by the faster roller)
3 = sheet sticks (is entrained by the faster roller)
4 = sheet sticks firmly (can only be peeled off with difficulty)
5 = sheet sticks very firmly (cannot be peeled off at all)
It may be seen from both Tables that, for the same total emulsifier content of the mixture (Examples 8 and 3, 9 and 4), the degree of tackiness on mixing rolls is identical, although stability in storage may be distinctly improved by the measures according to the present invention. Although an excessive emulsifier content (Examples 5, 6, 7) has a favourable effect upon the stability of the rubber in storage, it has a highly adverse affect upon tackiness on mixing rolls.

Vulcanisate testing

Production of the mixtures, vulcanisation and testing of the vulcanisates are carried out in accordance with ISO Specification No. 2475-1975 (E).

Before the mixture is actually produced, 1000 g of polychloroprene are masticated for 6 minutes, the gap between the rollers being adjusted to such a width that a bead approximately 12 mm in diameter is formed. After mastication, 800 g of rubber are removed and stored for at least 10 minutes and for at most 120 minutes.

Before the beginning of mixing, the mixing rolls adjusted to a temperature of 30°C. are heated by means of waste rubber to the indicated lower limit to the working temperature range. Test mixture

The mixing sequence and mixing times are as indicated. After mixing for 13 minutes, the rough sheet is sheared in opposite directions (3 times to the left and 3 times to the right) for 1 minute and then drawn 6 times over a period of 2 minutes through a 0.8 mm wide roller gap, giving a total mixing time of 16 minutes.

The mixture should have been stored for at least 15 hours (overnight) before vulcanisation.

The test data are determined in accordance with the corresponding DIN Specifications for soft rubber. A 4 mm thick R1 standard ring is used for determining strength, breaking elongation and modulus in accordance with DIN 53 504 and ISO 37-1976.